The Puy-les-Vignes breccia pipe (Massif Central, France): a unique occurrence of polymetallic W-Nb±Ta-HREE-Bi-Cu-As±Au-Ag mineralization in the Variscan belt

Matthieu Harlaux, Christian Marignac, Michel Cuney, Julien Mercadier

The Puy-les-Vignes breccia pipe (Massif Central, France): a unique occurrence of polymetallic W-Nb±Ta-HREE-Bi-Cu-As±Au-Ag mineralization in the Variscan belt

Matthieu Harlaux, Christian Marignac, Michel Cuney, Julien Mercadier
Université de Lorraine, CNRS, CREGU, GeoRessources, Vandoeuvre-lès-Nancy, F-54506, France.

Abstract. The Puy-les-Vignes deposit (Limousin, French Massif Central) represents an uncommon occurrence in the West European Variscan belt of a hydrothermal tungsten mineralization associated with a breccia pipe structure. A new study of this atypical quartz-wolframite-tourmaline deposit has been possible, allowing to revisit the mineral paragenesis and to identify four main successive stages of mineralization: (i) W-As-Nb±Ta stage corresponding to the historically economic mineralization hosted in quartz-wolframite-arsenopyrite veins; (ii) Fe-Cu-Zn±Mo stage represented by the deposition of base metal sulphides; (iii) Nb-Y-HREE stage associated with a late hydrothermal paragenesis in a tourmaline, adularia and chlorite matrix; (iv) Bi±Au-Ag stage, related to the late-Variscan regional metallogenic event in the Limousin.

Keywords.
Puy-les-Vignes; tungsten mineralization; breccia pipe; rare-metal; French Massif Central; Variscan belt.

1 Geological setting

The Puy-les-Vignes deposit is located in the northwestern part of the French Massif Central (FMC) in the Limousin area (Figure 1), which consists of a stack of metamorphic nappes emplaced during the continental collision between Gondwana and Laurussia through the Upper Paleozoic (Faure et al. 2009 and references therein). In France, the FMC is the largest area where Variscan terranes are exposed and has an important economic potential for the W-Sn and rare-metal deposits (Marignac & Cuney 1999, Cuney et al. 2002, Bouchot et al. 2005). The Puy-les-Vignes deposit was mined underground until 1957, producing around 4 kt WO_3, and was the second ranking tungsten mine in France during the XXth century. The mineralization is contained in a breccia pipe with dimensions 80 x 340 m at surface and at least 300 m in depth, possibly located at the apex of a hidden granite, as already described for other breccia pipes by Sillitoe (1985). The pipe is hosted in the biotite-sillimanite gneisses of the Lower Gneiss Unit (LGU), the intermediate nappe in the three nappes pile of the FMC, and cuts two dykes of leucogranites and lamprophyres (Weppe, 1951). The deposit is in the close vicinity of the Auriat granite (324±1 Ma, Gebauer et al. 1981) and the Aureil granite (346±14 Ma, Duthou 1978), which are peraluminous "S-type" granites, respectively of the Limousin- and Guéret-types of Stussi (1989) (Figure 1). The tungsten mineralization has been dated at 323±0.9 Ma by $^{40}Ar/^{39}Ar$ on muscovite associated with the wolframite (Cuney et al. 2002) and would therefore be coeval with the emplacement of the regional Limousin-type peraluminous leucogranitic complexes, such as St-Sylvestre and Millevaches. According to Weppe (1951, 1958), the Puy-les-Vignes pipe resulted from: (i) a first stage of collapsing leading to a quartz-matrix supported breccia, with metric to centimetric angular clasts of the country rocks (mainly gneisses and granites), which are systematically rimmed by an aureole of tourmalinite, of which the thickness varies from a few millimeters to ten centimeters, until up to the complete tourmalinization of the fragments; (ii) a "mass collapsing" underlined by planar-curved quartz veins ("plateures") within the breccia and quartz-filled decollements at the breccia to country rocks boundaries ("gaine"), which were the host for the economic mineralization, although the first breccia stage contains a potential low-grade tungsten mineralization.

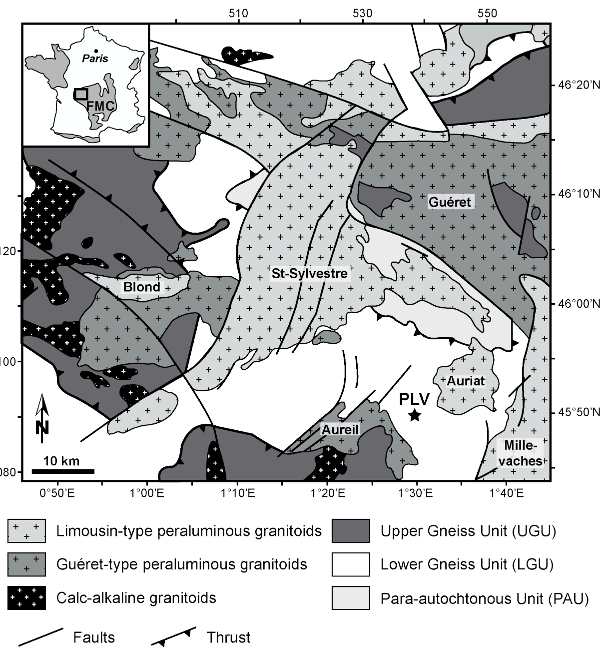

Figure 1. Location and geological setting of the Puy-les-Vignes (PLV) deposit in the Limousin area, French Massif Central (FMC).

2 Paragenetic sequence of the deposit

According to the descriptions of Alikouss (1993) and to new petrographic observations, the paragenetic sequence of the Puy-les-Vignes deposit can be divided into six main stages (Figure 2).

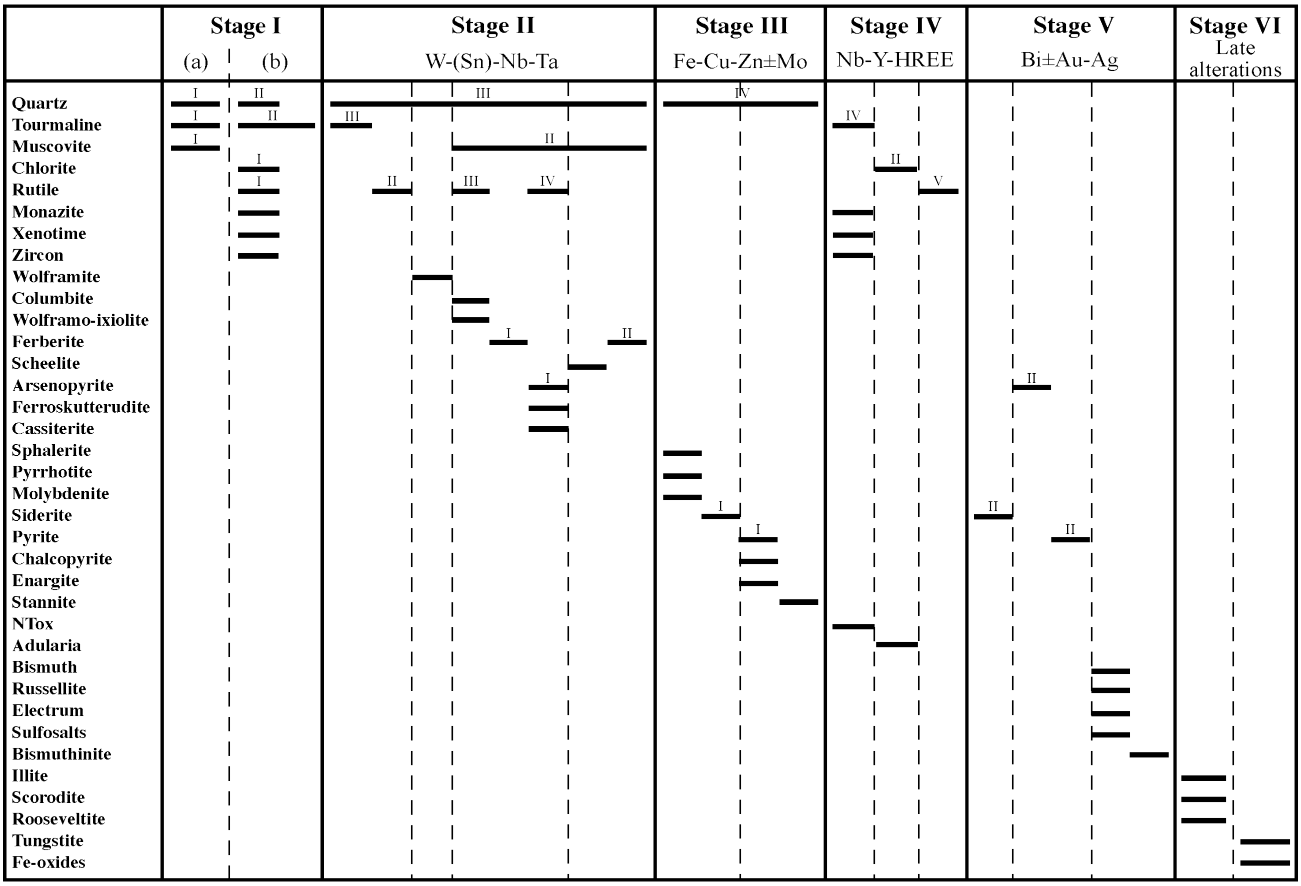

Figure 2. Paragenetic sequence of the Puy-les-Vignes deposit.

2.1 Stage I: Early hydrothermal alteration and brecciation

The country rocks are affected by a pervasive greisenization, destabilizing the primary feldspars and biotites and forming a secondary quartz-muscovite±tourmaline assemblage. The foliation is partially preserved within the gneissic clasts and relicts of biotites and feldspars remain in unaltered parts of the clasts, suggesting that the greisenization is diffuse within the country rocks and likely limited to early fissural discontinuities. Fluid overpressures lead to the hydraulic brecciation and collapse of the enclosing rocks, forming the breccia pipe. The clast rims are intensely tourmalinized, forming a recrystallization front (boron metasomatism), regardless of their lithology (greisenized gneisses or granites) (Figure 3a). There were two successive steps: (i) chloritization of the residual biotites, forming secondary anhedral crystals (50-100 µm) of Ti-W oxides (~3-5% W), coeval with the crystallization of minor monazite, xenotime and zircon, followed by tourmalinization of the greisen, resulting in a quartz-tourmaline assemblage (Figure 3b); (ii) massive tourmalinization of the clasts rims, forming a tourmalinite aggregate composed of elongated prisms of tourmalines with a palissadic structure (Figure 3b).

2.2 Stage II: W-As-Nb±Ta mineralization

Second stage brecciation leads to the infilling by milky quartz, forming the matrix of the breccia and cutting the tourmalinite rims (Figure 3a). The quartz contains the wolframite and arsenopyrite (Figure 3c), together with disseminated crystals of acicular tourmalines and muscovites. The wolframite forms euhedral prismatic crystals, millimetric to centimetric in size, growing onto tourmalinite, and sometimes broken and disseminated within latter quartz generation. Two types of accessory rare-metal oxides are associated to the wolframite within the quartz: (i) euhedral to sub-euhedral crystals (100-500 µm) of Ti-W oxides (~3-5% W), characterized by Nb (~15%) and Ta (~5%) bearing overgrowths with a patchy texture; (ii) sub-euhedral crystals (200-500 µm) of wolframo-ixiolite and Fe-columbite in microcavities infillings or in overgrowths on the quartz-cemented wolframite. The latter is partially replaced by ferberite 1 with a complex internal texture, along cracks or crystal borders, and crystallizing in overgrowth on wolframo-ixiolite. The arsenopyrite forms sub-euhedral crystals, which cut the wolframite within veinlets. Its deposition is coeval with the crystallization of minor cassiterite. The arsenopyrite is rich in Co (~4.5%) and Ni (~1%) and contains many inclusions, such as ferroskutterudite, pyrrhotite, wolframite, xenotime, monazite and rutile, the latter being particularly rich in Nb (up to 12%), Ta (up to 2.5%), W (up to 10%) or Cr (up to 6%). The presence of Co, Ni, Fe and Cr suggests the local contribution of a mafic or ultramafic source (*e.g.* lamprophyre dyke) during the crystallization of arsenopyrite. Scheelite occurs lately by replacement of the wolframite and ferberite 1, cutting the arsenopyrite within veins, and is itself replaced by ferberite 2 (so-called "reinite").

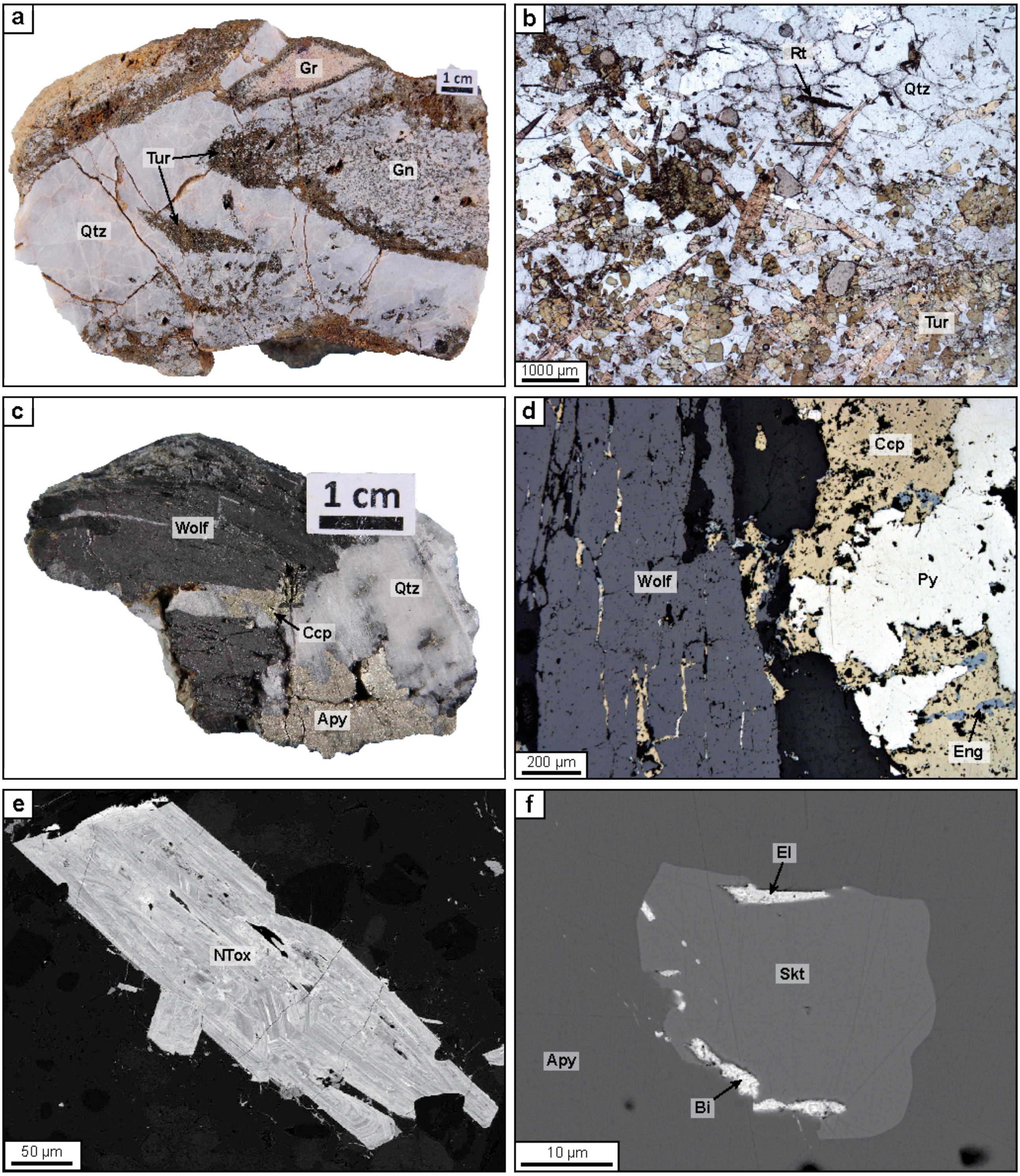

Figure 3. Photographs of samples from the Puy-les-Vignes deposit. (a) Clasts of greisenized gneisses (Gn) and granites (Gr) rimmed by an aureole of tourmalinite (Tur) and cemented within the milky quartz (Qtz) forming the matrix of the breccia pipe. (b) Microphotograph in transmitted light of the tourmalinite aureole formed by a quartz-tourmaline-rutile (Rt) assemblage, progressively passing to an aggregate of tourmaline crystals. (c) Sample of mineralized quartz vein containing an association of wolframite (Wolf) and arsenopyrite (Apy) with overgrowths of chalcopyrite (Ccp). (d) Microphotograph in reflected light showing an association of pyrite (Py), chalcopyrite (Ccp) and enargite (Eng) in overgrowths and infillings into the wolframite. (e) BSE image of a Nb-Ti-Y-HREE-W-U oxide (NTox), displaying complex internal textures, within a tourmaline-adularia-chlorite matrix. (f) BSE image of native bismuth (Bi) and electrum (El) infilling the ferroskutterudite (Skt) within arsenopyrite (Apy).

2.3 Stage III: Fe-Cu-Zn±Mo mineralization

An association of base metals (Fe-Cu-Zn±Mo) sulphides formed mainly by pyrite, chalcopyrite and sphalerite, with minor pyrrhotite, enargite, stannite and molybdenite, fills the microcracks and microcavities within the tourmalinite from the stage I and ore minerals from the stage II (Figure 3d). Sulphide deposition is accompanied by the recrystallization of the milky quartz along the wolframite and arsenopyrite.

2.4 Stage IV: Nb-Y-HREE mineralization

A late hydrothermal stage is associated to the formation of a crackle-breccia with a tourmaline-adularia-chlorite matrix, coeval with the crystallization of a series of accessory minerals comprising monazite, xenotime, zircon, Nb-Fe-W-rich rutile and Nb-Ti-Y-HREE-W-U oxides, referred to as NTox (Figure 3e). The latter are particularly rich in Nb (up to 30%), Y (up to 13%), HREE (up to 5%), W (up to 5%), U (up to 3%) and Ta (up to 1%), with uncommon chemical composition and complex internal textures.

2.5 Stage V: Bi±Au-Ag mineralization

A discrete mineralization of native bismuth, Bi-Ag-Se-Te sulphosalts and electrum (Au-Ag) fills microcavities and microcracks within the quartz, wolframite and arsenopyrite from the stage II and the base metal sulphides from the stage III (Figure 3f). This mineral paragenesis cuts also the adularia-chlorite-tourmaline matrix from the stage IV. An association of siderite, arsenopyrite and As-rich pyrite precedes the deposition of the Bi-phases. A rim of bismuthinite (Bi_2S_3) surrounds occasionally the native bismuth, indicating a progressive sulphidation of the latter. Ferberite 2 is locally transformed in russellite (Bi_2WO_6) at contact with native bismuth.

2.6 Stage VI: Late hydrothermal and supergene alterations

Late hydrothermal circulations are responsible for alteration of arsenopyrite in scorodite ($FeAsO_4.2H_2O$) and the crystallization of illite in residual microcavities within minerals of the previous stages. Scorodite veins contain in particular inclusions of rooseveltite ($BiAsO_4$), indicating the remobilisation of bismuth during the alteration of arsenopyrite. Finally, supergene alteration affects the ore body forming secondary minerals, such as tungstite ($WO_3.H_2O$) and Fe-oxides.

Conclusion

Four main successive stages of mineralization have been identified in the paragenetic sequence of the Puy-les-Vignes deposit: (i) a W-As-Nb±Ta stage associated with the deposition of quartz, wolframite, scheelite, arsenopyrite and rare-metal oxides in the hydrothermal veins through the breccia pipe; (ii) a Fe-Cu-Zn±Mo sulphide stage cutting the minerals of the previous stage; (iii) a Nb-Y-HREE stage, associated with a late hydrothermal paragenesis composed of zircon, xenotime, monazite, Nb-Fe-W-rich rutile and complex Nb-Ti-Y-HREE-W-U oxides (NTox), within an adularia-tourmaline-chlorite matrix; (iv) a Bi±Au-Ag stage, likely related to the late-Variscan regional hydrothermal circulations in the Limousin ca. 300 Ma (Bouchot et al. 2000, Boiron et al. 2003).

The peraluminous signature of the main W-As-Nb±Ta mineralization (stage II) contrasts with the late P, Y, HREE, Nb>Ta, Ti, Zr, U signature (stage IV), which would be more typical of a rare-metal peralkaline signature and could likely represent the contribution of peralkaline hydrothermal fluids derived from an unknown source at depth. In this respect, the Puy-les-Vignes breccia pipe appears unique in the West European Variscan belt.

Acknowledgements

This work was supported by the French National Research Agency through the national program "Investissements d'avenir" with the reference ANR-10-LABX-21-RESSOURCES21. The authors are thankful to Bernard Mouthier for access to the samples and to the field, and to Sandrine Mathieu, Lise Salsi and Olivier Rouer (GeoRessources, Vandœuvre-lès-Nancy, France) for technical support in providing analytical data.

References

Alikouss S (1993) Contribution à l'étude des fluides crustaux : approche analytique et expérimentale. Thèse INPL, Nancy, 255 p.

Boiron M-C, Cathelineau M, Banks DA, Fourcade S, Vallance J (2003). Mixing of metamorphic and surficial fluids during the uplift of the Hercynian upper crust: consequences for gold deposition. Chem Geol 194 :119–141.

Bouchot V, Milesi J-P, Ledru P (2000). Crustal scale hydrothermal palaeofield and related Au, Sb, W orogenic deposits at 310-305 Ma (French Massif Central, Variscan Belt). SGA News 10:6–12.

Bouchot V, Ledru P, Lerouge C, Lescuyer J-L, Milesi J-P (2005). Late Variscan mineralizing systems related to orogenic processes: The French Massif Central. Ore Geol Rev 27:169-197.

Cuney M, Alexandrov P, Le Carlier de Veslud C, Cheilletz A, Raimbault L, Ruffet G, Scaillet S (2002). The timing of W-Sn-rare metals mineral deposit formation in the Western Variscan chain in their orogenic setting: the case of the Limousin area (Massif Central, France). In: Blundell D.J, Neubauer F, Von Quadt A (eds) 2002. The Timing and Location of Major Ore Deposits in an Evolving Orogen. Geological Society, London, Special Publications 204:213-228.

Duthou J (1978). Les granitoïdes du Haut Limousin (Massif central français) chronologie Rb/Sr de leur mise en place; le thermo-métamorphisme carbonifère. B Soc Geol Fr 20:229-235.

Faure M, Lardeaux J-M, Ledru P (2009). A review of the pre-Permian geology of the Variscan French Massif Central. CR Geosci 341:202–213.

Gebauer H, Bernard-Griffiths J, Gnünenfelder M (1981). U/Pb zircon and monazite dating of mafic-ultramafic complex and its country rocks. Example: Sauviat-sur-Vige, French Massif Central. Contrib Mineral Petr 76:292-300.

Marignac C, Cuney M (1999). Ore deposits of the French Massif Central: insight into the metallogenesis of the Variscan collision belt. Miner Deposita 34:472-504.

Sillitoe R (1985). Ore-related breccias in volcanoplutonic arcs. Econ Geol 80:1467-1514.

Stussi J-M (1989). Granitoid chemistry and associated mineralization in the French Variscan. Econ Geol 84:1363-1381.

Weppe M (1951). Contribution à l'étude des gîtes de tungstène français : Puy-les-Vignes (Haute Vienne), La Châtaigneraie (Cantal). *Revue de Géologie appliquée et de Prospection minière, Société d'Impressions Typographiques, Nancy*, 210 p.

Weppe M (1958). Contribution à la géologie minière et à la minéralogie minière. Les gisements de wolfram de Leucamp, Puy-les-Vignes, Montbelleux. *Société d'Impressions Typographiques, Nancy*, 196 p.